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## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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<b>(21) International Application Number:</b> PCT/GB94/01427 <b>(22) International Filing Date:</b> 1 July 1994 (01.07.94) <b>(30) Priority Data:</b> 9313723.0 2 July 1993 (02.07.93) GB <b>(71) Applicant (for all designated States except US):</b> ZENECA LIMITED [GB/GB]; 15 Stanhope Gate, London W1Y 6LN (GB). <b>(72) Inventors; and</b> <b>(75) Inventors/Applicants (for US only):</b> MCLEAN, Colin, Henry [GB/GB]; 5 Dunlin Close, Beechwood, Runcorn, Cheshire WA7 3JR (GB). GREGORY, Peter [GB/GB]; 129 Armadale Road, Bolton BL3 4UN (GB). <b>(74) Agents:</b> MAYALL, John et al.; Zeneca Specialties, Intellectual Property Group, P.O. Box 42, Hexagon House, Blackley, Manchester M9 8ZS (GB).		<b>(81) Designated States:</b> AT, AU, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, ES, FI, GB, GE, HU, JP, KE, KG, KP, KR, KZ, LK, LU, LV, MD, MG, MN, MW, NL, NO, NZ, PL, PT, RO, RU, SD, SE, SI, SK, TJ, TT, UA, US, UZ, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> METHOD OF FORMING A THREE-DIMENSIONAL COLOURED ARTICLE		
<b>(57) Abstract</b>  A method of forming a three-dimensional article having at least one selectively coloured zone, said method comprising the steps of: (1) subjecting successive layers of a liquid photopolymerisable resin composition containing a colour former, a developer and an infrared absorber, to a programmed beam of electromagnetic radiation of a wavelength outside the infrared region of the spectrum thereby effecting polymerisation of the photopolymerisable resin composition to form successive layers of solid substantially polymerised resin composition and wherein adjacent layers become cohesively integrated as they are formed such that they define the structure of the three-dimensional article, and (2) subjecting the photopolymerisable resin or each layer of the solid substantially polymerised resin composition to a programmed beam of infrared light thereby effecting colour development or colour change in one or more zones in the article.		

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## METHOD OF FORMING A THREE-DIMENSIONAL COLOURED ARTICLE.

This invention relates to a process and more particularly to a method for the production of three-dimensional articles in which selected parts are coloured in order to provide visible differentiation from other parts of the article.

5       Methods are known for generating three-dimensional models by the selective application of programmed beams of electromagnetic radiation to a fluid medium comprising a photopolymerisable resin composition which becomes selectively cured to form the desired structure.

10       In particular, US Patent No.4,575,330 describes the method known as "stereolithography". Briefly, stereolithography is a method for making solid articles by successively "printing" thin layers of a radiation-curable material, one on top of the other. A programmed movable spot beam of electromagnetic radiation, for example a laser beam, focused into a surface or layer of radiation curable liquid is used to form a solid cross-section of  
15 the article at the surface of the liquid. The cross-section so obtained is then moved, in a programmed manner, away from the liquid surface and into the liquid by the thickness of one layer and the next cross-section is then formed and adhered to the immediately preceding layer. This operation is repeated until the entire article, consisting of a plurality of cohesively  
20 integrated cross-sections is formed. The formed article may then be subjected, if necessary and/or desired, to a post-cure to minimise residual unpolymerised material. The technique allows the rapid construction of complex shaped, three-dimensional articles without the need for expensive tooling equipment or moulds, especially objects containing voids or having  
25 irregular shapes.

In principle, a three-dimensional model is constructed in a computer file (CAD/CAM), sliced into cross-sectional elements or layers, and a computer then directs a light source to image each cross-sectional element, one on top of the other, in a resin tank to produce a solid laminated model  
30 of the computer image. For medical applications, CT or MRI scanning can be used to generate the initial data as proposed in EP-A-0348061.

In some situations, it would be advantageous if parts of a three-dimensional article obtained by stereolithography could be visually differentiated from other parts thereof. This could be especially useful in  
35 anatomical and medical models for teaching purposes and more particularly in models of parts of the anatomy of human patients in order to differentiate between different tissue types, for example between bone and tumour tissue and thereby assist in the interpretation of the model prior to invasive surgery.

40       It has now been found that such visual differentiation can be provided by carrying out the stereolithographic process on a polymerisable resin

composition containing an infra red absorber which, in conjunction with a colour former and developer, causes colour development or colour change on activation by infra red light.

Thus, according to the invention, there is provided a method of forming  
5 a three-dimensional article having at least one selectively coloured zone, said method comprising the steps of:

(1) subjecting successive layers of a liquid photopolymerisable resin composition containing a colour former, a developer and an infra red absorber, to a programmed beam of electromagnetic radiation of a wavelength  
10 outside the infra red region of the spectrum thereby effecting polymerisation of the photopolymerisable resin composition to form successive layers of solid substantially polymerised resin composition and wherein adjacent layers become cohesively integrated as they are formed such that they define the structure of the three-dimensional article, and

15 (2) subjecting the photopolymerisable resin or each layer of the solid substantially polymerised resin composition to a programmed beam of infra red light thereby effecting colour development or colour change in one or more zones in the article.

The electromagnetic radiation referred to in Step (1) above is  
20 preferably ultraviolet or visible electromagnetic radiation. Step (2) may be performed before, during or after Step (1), preferably after Step (1). The article is preferably a model, more preferably an anatomical or medical model.

In a second aspect of the invention, there is provided a method of  
25 forming a three-dimensional model having at least one selectively coloured zone corresponding to at least one physically differentiated zone present in an original three-dimensional article, said method comprising the steps of:

(1) subjecting successive layers of a liquid photopolymerisable resin composition, containing a colour former, a developer and an infra red  
30 absorber, to a programmed beam of ultraviolet or visible electromagnetic radiation capable of effecting polymerisation of the photopolymerisable resin composition whereby to form successive layers of solid substantially polymerised resin composition and wherein adjacent layers become cohesively integrated as they are formed such that they define the structure of the  
35 three-dimensional model, and

(2) subjecting each layer of the solid substantially polymerised resin composition, before polymerisation of the succeeding layer of liquid photopolymerisable resin composition, to a programmed beam of infra red light thereby effecting colour development or colour change in one or more zones in  
40 the model corresponding to one or more physically differentiated zones present in the three-dimensional article.

The present invention is particularly useful for preparing three-dimensional models of joints and bones, e.g. those found in toes, feet, legs,

hips, pelvis, ribs, the spinal column, arms, hands, fingers, head (particularly the cranium, jaw and teeth) and of organs, e.g. the heart, lungs, kidney and liver.

The three-dimensional model or reproduction formed in the method of the invention may be substantially identical in size with the original three-dimensional article or it may be smaller or larger according to convenience.

The "physically differentiated" zones present in the original three dimensional article are zones which should differ in some physically detectable property, for example density or X-ray absorptivity, from other parts of the article. In particular, these physically differentiated zones should be detectable and distinguishable by the original data collection/production apparatus, for example CT or MRI scanning.

The selectively coloured zones present in the reproduction may be such that parts of the resultant model or article are coloured whilst other parts are substantially uncoloured or such that parts have one colour whilst the other parts have another colour. Differences in colour intensity are also possible.

The photopolymerisable resin composition used in the method of the invention may, apart from the presence of a colour former, developer and infra red absorber, be of a conventional type, such compositions having been fully described in the prior art. Suitable compositions contain a photopolymerisable compound or a mixture of such compounds, the term "photopolymerisable compound" embracing monomeric, oligomeric and polymeric compounds which can be photopolymerised under the influence of a photoinitiator. Examples of photopolymerisable compounds are organic compounds containing groups polymerisable by free radicals and/or cationically polymerisable groups.

Compounds polymerisable by free radicals include compounds containing at least one ethylenically unsaturated group per molecule, especially the acrylate and/or methacrylate group. Such compounds may be used in conjunction with free radical generating photoinitiators, for example aromatic ketones,  $\alpha$ -diketones, thioxanthenes, acylphosphine oxides, onium salts and the like. In many cases, the efficiency of the free radical photoinitiators may be improved by the inclusion of an amine, especially a tertiary amine such as dimethylaminoethyl methacrylate or ethyl p-dimethylaminobenzoate.

In a preferred embodiment the photopolymerisable resin comprises (apart from the colour former, developer and infra red absorber) the resins described in Canadian Patent Application 2028541A1, particularly Claim 1 which is incorporated herein by reference thereto.

Preferably the liquid photopolymerisable resin composition has a viscosity of 200 to 2000 mPas at 30°C.

Compounds capable of cationic polymerisation include epoxy compounds, especially compounds containing at least two epoxy groups per molecule, cyclic ethers, lactones, cyclic acetals, cyclic thioethers, vinyl compounds and the like. Cationic photoinitiators which may be used in conjunction with  
5 such compounds include onium salts which are double salts capable of releasing a Lewis acid when irradiated by an energy beam.

Examples of photopolymerisable resin to which the colour former, developer and infra red absorber are added are described in patent specifications EP 425441, EP 525578, EP 492953, WO 92/15620, WO 89/08021, EP  
10 430992, EP 378144, EP 425440, EP 562826, EP 554215, EP 536086 and EP 506616.

Substantially colourless colour formers used in conjunction with solid developers which, when caused to melt, for example by exposure to infrared radiation, react with the colour formers to produce coloured substances. Melting of the developer is facilitated by incorporating an infrared absorber  
15 which converts the radiation energy into thermal energy.

In one embodiment the colour change is irreversible thus allowing the model to be stored without fear of loss of colour from the coloured zones.

Preferably the colour former is colourless or weakly coloured. Suitable colour formers are basic dyes which, when heated with a developer,  
20 change colour or produce colour. Especially preferred colour formers include triaryl methane-, diphenyl methane-, thiazine-, spiro-, lactam- and fluoran-based colour formers. Examples of Triarylmethane-based colour formers include, 3,3-bis(p-dimethylaminophenyl)-6-dimethylaminophthalide, 3,3-bis(p-dimethylaminophenyl)phthalide, 3-(p-dimethylaminophenyl)-3-(1,2-  
25 dimethylindole-3-yl)phthalide, 3-(p-dimethylaminophenyl)-3-(2-methylindole-3-yl)phthalide, 3,3-bis(1,2-dimethylindole-3-yl)-5-dimethylaminophthalide, 3,3-bis(1,2-dimethylindole-3-yl)-6-dimethylaminophthalide, 3,3-bis(9-ethylcarbazole-3-yl)-6-dimethylaminophthalide, 3,3-bis(2-phenylindole-3-yl)-6-dimethylaminophthalide, 3-p-dimethylaminophenyl-3-(1-methylpyrrole-3-yl)-6-  
30 dimethylaminophthalide, etc, especially Crystal Violet Lactone.

Diphenylmethane-based colour formers include 4,4'-bis-dimethylaminobenzhydryl benzyl ether, N-halophenyl-leucoauramine and N-2,4,5-trichlorophenyl-leucoauramine.

Thiazine-based colour formers include benzoyl-leucomethylene blue and  
35 p-nitrobenzoyl-leucomethylene blue.

Spiro-based colour formers include 3-methyl-spiro-dinaphthopyran, 3-ethyl-spiro-dinaphthopyran, 3-phenyl-spirodinaphthopyran, 3-benzyl-spiro-dinaphthopyran, 3-methyl-naphtho-(6'-methoxybenzo)spiropyran and 3-propyl-spiro-dibenzopyran.

40 Lactam-based colour formers include rhodamine- $\beta$ -anilinolactam, rhodamine-(p-nitroanilino)lactam and rhodamine-(o-chloroanilino)lactam.

Fluoran-based colour formers include 3,6-dimethoxyfluoran, 3,6-diethoxyfluoran, 3,6-dibutoxyfluoran, 3-dimethylamino-7-methoxyfluoran, 3-



- dimethylamino-6-methoxyfluoran, 3-dimethylamino-7-methoxyfluoran, 3-diethylamino-7-chlorofluoran, 3-diethylamino-6-methyl-7-chlorofluoran, 3-diethylamino-6,7-dimethylfluoran, 3-(N-ethyl-p-toluidino)-7-methylfluoran, 3-diethylamino-7-(N-acetyl-N-methylamino)fluoran, 3-diethylamino-7-N-methylaminofluoran, 3-diethylamino-7-dibenzylaminofluoran, 3-diethylamino-5-methyl-7-dibenzylaminofluoran, 3-diethylamino-7-(N-methyl-N-benzylamino)fluoran, 3-diethylamino-7-(N-chloroethyl-N-methylamino)fluoran, 3-diethylamino-7-diethylaminofluoran, 3-(N-ethyl-p-toluidino)-6-methyl-7-phenylaminofluoran, 3-(N-ethyl-p-toluidino)-6-methyl-7-phenylaminofluoran, 3-diethylamino-7-(2-carbomethoxy-phenylamino)fluoran, 3-(N-ethyl-N-isoamylamino)-6-methyl-7-phenylaminofluoran, 3-(N-cyclohexyl-N-methylamino)-6-methyl-7-phenylaminofluoran, 3-pyrrolidino-6-methyl-7-phenylaminofluoran, 3-piperidino-6-methyl-7-phenylaminofluoran, 3-diethylamino-6-methyl-7-xylidinofluoran, 3-diethylamino-7-(o-chlorophenylamino)fluoran, 3-dibutylamino-7-(o-chlorophenylamino)fluoran and 3-pyrrolidino-6-methyl-7-p-butylphenylaminofluoran.

Colour formers permitting the production of a wide range of colours are known and have been described, for example, by Peter Gregory in High-Technology Applications of Organic Colourants, Plenum Press, pages 124-134.

- Especially suitable colour formers include triphenylmethane derivatives such as Crystal Violet Lactone and various xanthene type compounds.

- Preferred developers have a melting point above 40°C, more preferably above 60°C. The developers which assist the colour formation are preferably inorganic or organic acidic materials. Inorganic acidic materials include activated clay, acidic clay, attapulgit, bentonite, colloidal silica and aluminum silicate, Organic acidic materials include phenolic compounds, especially 4-tert-butyl-phenol, bisphenol A, 4-tert-octylphenol, 4-phenylphenol, 4-acetylphenol,  $\alpha$ -naphthol,  $\beta$ -naphthol, hydroquinone, 2,2'-dihydroxydiphenyl, 2,2'-methylenebis-(4-methyl-6-tert-butylphenol), 2,2'-methylenebis-(4-chlorophenol), 4,4'-dihydroxy-diphenylmethane, 4,4'-isopropylidenediphenol, 4,4'-isopropylidenebis-(2-tert-butylphenol), 4'-sec-butylidenediphenol, 4,4'-cyclohexylidenediphenol, 4,4'-dihydroxydiphenyl sulfide, 4,4'-thiobis-(6-tert-butyl-3-methylphenol), 4,4'-dihydroxydiphenyl sulfone, 4-hydroxybenzoic acid benzylester, 4-hydroxyphthalic acid dimethylester, hydroquinone monobenzyl ether, novolak phenol resins and phenolic polymers; aromatic carboxylic acids such as benzoic acid, p-tert-butylbenzoic acid, trichlorobenzoic acid, 3-sec-butyl-4-hydroxybenzoic acid, 3-cyclohexyl-4-hydroxybenzoic acid, 3,5-dimethyl-4-hydroxybenzoic acid, salicylic acid, 3-isopropylsalicylic acid, 3-tert-butylsalicylic acid, 3-benzylsalicylic acid, 3-( $\alpha$ -methylbenzyl)salicylic acid, 3-chloro-5-( $\alpha$ -methylbenzyl)salicylic acid, 3,5-di-tert-butylsalicylic acid, 3-phenyl-5-( $\alpha$ , $\alpha$ -dimethylbenzyl)salicylic acid, 3,5-di-( $\alpha$ -methylbenzyl)salicylic acid and terephthalic acid; also, salts of such phenolic compounds and aromatic

carboxylic acids, particularly with polyvalent metals such as zinc, magnesium, aluminum, calcium, titanium, manganese, tin or nickel.

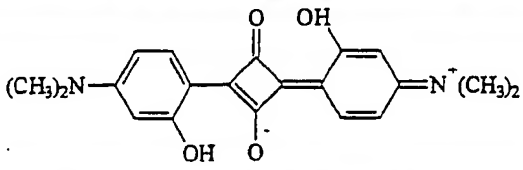
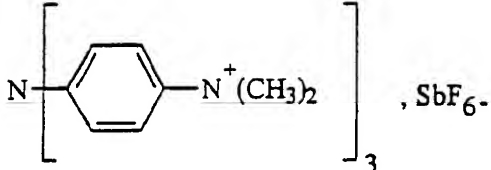
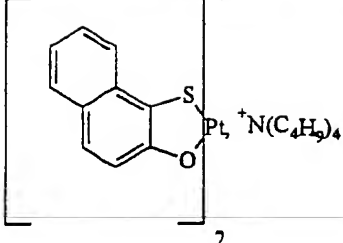
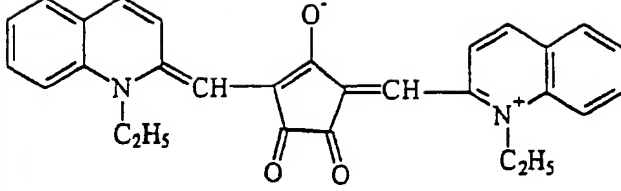
The infra red absorber preferably has an absorption maximum at above 700nm, more preferably above 750nm, especially in the range 750nm-2000nm.

5 The infra-red absorber may be inorganic but it is preferably organic.

Inorganic infra red absorbers include aluminium oxide and hydroxide; silicate minerals such as the olivine group; including olivine, garnet group including almandine and spessartine, pyroxene group including enstatite, amphibole group including tremolite and actinolite, mica group including muscovite and biotite, feldspar group including oligoclase and anorthite, silica mineral group including quartz and cristobalite, clay minerals including kaolinite and montmorillonite, etc.; zinc silicate, magnesium silicate, calcium silicate barium silicate, zinc phosphate, trisilicon tetranitride & boron nitride, barium sulfate, calcium sulfate, and strontium sulfate; calcium carbonate, barium carbonate, magnesium carbonate, zinc carbonate and potassium nitrate.

Suitable organic infra red absorbers include metal dithienes, metal dithiolenes, metal mercaptophenols, benzoquinones, naphthoquinones, anthraquinones, phthalocyanines (especially aryloxy and aryl thio phthalocyanines) and triarylphosphates and compounds of the nitroso, cyanine, nigrosine, imminium, diiminium, squarilium, croconium, quinone, azo, indoaniline, azulenium, pyrilium, thiapyrilium series.

Examples of organic infra red absorbers include the following:

STRUCTURE	TYPE	Lambda MAX (nm)
	Squarilium	700
<p>5</p> 	Imminium	920
	Mercaptophenol	1200
CuPc (S-Ph-CH <sub>3</sub> ) <sub>15/16</sub>	Phthalocyanine	770
	Croconium	845

Further examples of organic infra red absorbers are given in the above mentioned book by Peter Gregory, pages 219-243, which are incorporated herein by reference thereto. Patent specifications EP 135995, EP 155780, EP 282181, US4824947, US 4824948, EP 340898, US 5189153 and EP 484018 of ZENECA Limited describe still further infra red absorbers and certain of these compounds are commercially available under the trade mark PRO-JET. Mitsui Toatsu also sell organic infra red absorbers.

The function of the infra red absorber is to absorb radiation from the beam of infra red light and, as a result, heat the colour former and developer thereby causing a chemical reaction to occur which effects colour development or colour change. Thus one will choose an infra red absorber which strongly absorbs the frequency of infra red light which is used. Table 1 below shows the absorption wavelengths of various inorganic infra red absorbers and is a useful guide for selecting compatible absorbers and light sources.

TABLE 1

	<u>Infra red absorber</u>	<u>Absorption Wavelength (<math>\mu\text{m}</math>)</u>
	$\text{Zn}_2\text{SiO}_4$	10.6
	$\text{BaSO}_4$	9.2
20	Talc*	9.6
	$\text{CaMgSiO}_4$	10.2
	$\text{Ba}_2\text{MgSi}_2\text{O}_7$	10.3 or 10.6
	$\text{BaZn}_2\text{Si}_2\text{O}_7$	10.2 or 10.6
	$\text{Sr}_2\text{SiO}_4$	10.3 or 10.7
25	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	9.2

\*finely divided talc (Trademark "MISTRON VAPOR", available from Nihon Mistron Co. Ltd. Japan).

The photopolymerisable resin may also contain a sensitiser which improves the sensitivity of the colour former for the developer resulting in a stronger coloration. Examples of such sensitisers include dimethyl terephthalate and O-chloro-N-propionamido aniline which work particularly well when the developer is bisphenol A.

The liquid photopolymerisable resin preferably contains 0.1 to 10%, more preferably 0.1 to 5% colour former (especially 0.2 to 2%); 1 to 25%, more preferably 1 to 16% developer (especially 1.5 to 15%); and 0.01 to 10%, preferably 0.01 to 5% infra red absorber (especially 0.02 to 1%). When a sensitiser is used this is preferably present in an amount of up to 2%.

Suitable infrared absorbers for inclusion with the colour formers and solid developers have also been described in the prior art, for example in our EP-A-0155780, EP-A-0282181 and EP-A-0282182 and at pages 218-243 of the above mentioned book by Peter Gregory.

The photopolymerisable resin composition may also contain other conventional ingredients, for example organic or inorganic fillers for

modification of the final physical and/or mechanical properties of the model.

Polymerisation of the photopolymerisable resin composition by the application of electromagnetic radiation outside of the infra red, especially ultra violet or visible electromagnetic radiation, may be effected using  
5 conventional stereolithographic techniques in a manner fully described in the prior art. In order to form an article having selectively coloured zones, it is important that the first programmed beam of electromagnetic radiation is of such wavelength that it does not promote colour development or colour change to any significant extent. It is also important that the  
10 photopolymerisation is not sufficiently exothermic to cause solid developer to melt. Suitable operating conditions can be established by appropriate choice of developer and infrared absorber.

Suitable light sources for Step (1) include lasers such as argon ion lasers, helium-cadmium lasers and the like and also conventional light  
15 sources for generating ultra violet radiation or visible light such as extra high pressure mercury lamps, high pressure mercury lamps, medium pressure mercury lamps, metal halide lamps, xenon lamps, tungsten lamps and the like.

The infra red light beam may be applied to the photopolymerisable resin composition or "substantially polymerised" resin composition before, during  
20 or after photopolymerisation has been effected. When applied after photopolymerisation gelation of the resin composition has preferably reached such a stage that there is no significant diffusion of colour from coloured to uncoloured zones, due to mobility of the reactants caused by diffusion or by thermally induced mobility. The infra red light beam may therefore be  
25 applied on a layer by layer basis as the article is formed by scanning the whole or selected parts of each layer or it can follow the first step throughout the curing operation with an appropriate time lag.

The infra red light beam may be programmed in manner analogous to the known manner so as to be activated only in response  
30 to selected physical features present in the original three-dimensional object, for example zones of higher or lower density than the remainder of said object or of different material composition. Thus, for example, for the preparation of an anatomical model, data obtained of part of the human anatomy by body-scanning equipment and representative of different tissue  
35 types may be converted in known manner into computer data capable of programming the beam of radiation.

The present invention also provides use of a photopolymerisable resin composition containing a colour former, a developer and an infra red absorber to form a three-dimensional model having at least one selectively coloured  
40 zone corresponding to at least one physically differentiated zone present in an original three-dimensional object.

The preferred colour former, developer and infra red absorber are as hereinbefore described and the model is preferably a medical or anatomical model as discussed above.

The wavelength of the infra red light beam will be such as to effect colour development or colour change and, therefore, will be different from the wavelength of the first programmed beam of electromagnetic radiation used in Step (1).

Thus it is convenient to use visible light for Step (1) and infra red light for Step (2). Suitable infra red lasers include gallium-aluminium-arsenide (GaAlAs) lasers (780-830nm) and the more powerful neodymium yttrium-aluminium-garnet (Nd-YAG) (1064nm), GaAs lasers (780-905nm), GaAs x P<sub>1-x</sub> (650-900nm), InP lasers (900nm), InGaP Lasers (760nm), Nd:YLF lasers (1047/1053nm) and Nd:YAP Lasers (1080nm) and CO<sub>2</sub> lasers.

The invention is further illustrated by the following examples in which all parts and percentages are by weight unless specified otherwise.

Infra red absorber (IRA) Y had the formula CuPc(-S-[2-naphthyl])<sub>15/16</sub> and (IRA) Z had the formula CuPc(-S-[4-methylphenyl])<sub>10</sub>(-S-[4-methoxyphenyl])<sub>5</sub>. PRO-JET 900 NP is an IRA available from ZENECA Limited, Blackley, Manchester, England.

Crystal Violet Lactone is a commercially available Colour former and bisphenol A is available from Aldrich Chemical Company Ltd, Gillingham, England.

Resin X was prepared by mixing ethoxylated bisphenol A dimethacrylate ester (DIACRYOL 101, obtained from Akzo chemicals, 45g) with NeoRad NR 2720 having a molecular weight of 950 and viscosity of 1200 mPas at 25°C, (24g, obtained from ZENECA Resins, USA), polyethylene glycol (400) diacrylate (SR 344 obtained from Sartomer Company), alkoxylated triacrylate having a molecular weight of 1000 (SR9035, obtained from Sartomer Company, 10.5g) and 1,1-dimethyl-1-hydroxy acetophenone (5.5g). Resin X is a clear liquid having a viscosity of 388 mPas at 30°C.

#### Example 1

This example shows the importance of an infra red absorber being present in the photopolymerisable resin composition. Compositions A and B were prepared having the ingredients shown in Table 1 below. A film was formed by curing a 100µm layer of the composition with an ultra violet light Fusion "D" lamp, (300W, 3J/cm<sup>2</sup>) and the cured film was irradiated with infra red light (a laser diode from Spectra (Physics) Ltd, 820nm, power 100mW).

The "impression" describes, qualitatively, response of the film to the infra red source. Zero means there was no response, 2 and 3 was a good response and 5 means the film burned through (an excessive response).

The "Colour" indicates the intensity of colour formed. Zero means no colour formation, 10 means extremely intense colour formation, and numbers in between indicate colour intensity between these two extremes.

Table 1

INGREDIENTS	(Amounts in Percent)	
	A	B
Resin X	85.00	85.00
Colour Former (Crystal Violet Lactone)	1.50	1.50
5 Colour Developer (Bisphenol A)	13.30	13.30
Infra-red Absorber Y	0	0.15

## Laser Imaging Results

	: Impression	0	3
10	: Colour	0	7

Example 2

This example compares the effects of different infra red absorbers on impression and colour. The compositions were prepared, cured with ultraviolet and irradiated with infra red as described in Example 1.

15 Table 2

Ingredients	(Amounts in percent)		
	C	D	E
Resin X	85.20	85.20	85.20
Colour Former (Crystal Violet Lactone)	1.10	1.00	1.00
Colour Developer (Bisphenol A)	13.30	13.30	13.30
20 Infra-red Absorber PRO-JET 900NP	0.50	0	0
Infra-red Absorber Y	0	0.50	0
Infra-red Absorber Z	0	0	0.5

## Laser Imaging Results

25	: Impression	4	3	3
	: Colour	7	6	6

Example 3

This Example illustrates the effect of different levels of infra red absorber in the photopolymerisable resin composition. The compositions were prepared, cured with ultra violet and irradiated with infra red as described in Example 1.

30

Table 3

Ingredients	(Amounts in percent)	
	F	G
Resin X	86.05	85.70
Colour Former (Crystal Violet Lactone)	0.50	0.50
Colour Developer (Bisphenol A)	13.30	13.30
Infra-red Absorber Y	0.15	0.50

## Laser Imaging Results

	:	Impression	5	4
10	:	Colour	1	6

Example 4

This Example illustrates the effect of different levels of colour former in the photopolymerisable resin composition. The compositions were prepared, cured with ultra violet and irradiated with infra red as described in Example 1.

Table 4

Ingredients	(Amounts in percent)		
	H	I	J
Resin X	85.90	85.50	84.70
Colour Former (Crystal Violet Lactone)	0.60	1.00	1.80
Colour Developer (Bisphenol A)	13.30	13.30	13.3
Infra-Red Absorber Y	0.20	0.20	0.2

## Laser Imaging Results

	:	Impression	2	2	3
25	:	Colour	3	4	6

Example 5

This example illustrates the effect of using a sensitiser in the photopolymerisable resin composition which improves colour development. The compositions were prepared, cured with ultra violet and irradiated with infra red as described in Example 1.



Table 5

Ingredients	(Amounts in percent)	
	K	L
Cibatool XB 5149*	97.71	97.62
Colour Former (Crystal Violet Lactone)	0.51	0.51
5 Colour Developer (Bisphenol A)	1.52	13.30
Infra-red Absorber Y	0.26	0.25
Sensitiser (Dimethyl Terephthalate)	0	0.10

## Laser Imaging Results

10	:	Impression	1	4
	:	Colour	0	3

\* A resin available from Ciba Geigy AG, Switzerland.

CLAIMS

1. A method of forming a three-dimensional article having at least one selectively coloured zone, said method comprising the steps of:

5 (1) subjecting successive layers of a liquid photopolymerisable resin composition containing a colour former, a developer and an infra red absorber, to a programmed beam of electromagnetic radiation of a wavelength outside the infra red region of the spectrum thereby effecting polymerisation of the photopolymerisable resin composition to form successive layers of  
10 solid substantially polymerised resin composition and wherein adjacent layers become cohesively integrated as they are formed such that they define the structure of the three-dimensional article, and

(2) subjecting the photopolymerisable resin or each layer of the solid substantially polymerised resin composition to a programmed beam of infra red  
15 light thereby effecting colour development or colour change in one or more zones in the article.

2. A method of forming a three-dimensional model said model having at least one selectively coloured zone corresponding to at least one physically  
20 differentiated zone present in an original three-dimensional article, said method comprising the steps of:

(1) subjecting successive layers of a liquid photopolymerisable resin composition, containing a colour former, a developer and an infra red absorber, to a programmed beam of ultraviolet or visible electromagnetic  
25 radiation capable of effecting polymerisation of the photopolymerisable resin composition whereby to form successive layers of solid substantially polymerised resin composition and wherein adjacent layers become cohesively integrated as they are formed such that they define the structure of the three-dimensional model, and

30 (2) subjecting each layer of the solid substantially polymerised resin composition, before polymerisation of the succeeding layer of liquid photopolymerisable resin composition, to a programmed beam of infra red light thereby effecting colour development or colour change in one or more zones in the model corresponding to one or more physically differentiated zones  
35 present in the three-dimensional article.

3. A method according to Claim 1 or Claim 2 wherein the infra red absorber has an absorption maximum in the range 750nm-2000nm.

40 4. A method according to any one of the preceeding claims wherein the infra red absorber is inorganic.

5. A method according to Claim 1, 2 or 3 wherein the infra red absorber is organic.

6. A method according to Claim 1, 2 or 5 wherein the infra red absorber is selected from metal dithienes, metal dithiolenes, metal mercaptophenols, benzoquinones, naphthoquinones, anthraquinones, phthalocyanines, triarylphosphates and compounds of the nitroso, cyanine, nigrosine, imminium, diiminium, squarilium, croconium, quinone, azo, indoaniline, azulanium, pyrilium and thiapyrilium series.

10

7. A method according to any one of the preceeding claims wherein the colour former is a triaryl methane-, diphenyl methane-, thiazine-, spiro-, lactam-, or fluoran-based colour former.

15 8. A method according to any one of the preceeding claims wherein the developer is an inorganic or organic acidic material.

9. A method according to any one of the preceeding claims where the developer is a phenolic compound, an aromatic carboxylic acid, or a salt thereof.

20

10. A method according to any one of the preceeding claims wherein the photopolymerisable resin contains a sensitiser which improves the sensitivity of the colour former for the developer.

25

11. A method according to Claim 2 wherein the model is an anatomical or medical model.

12. A method according to any one of the preceeding claims where the liquid photopolymerisable resin contains 0.1 to 5% colour former, 1 to 16% developer and 0.01 to 5% infra red absorber.

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13. Use of a photopolymerisable resin composition containing a colour former, a developer and an infra red absorber to form a three-dimensional model having at least one selectively coloured zone corresponding to at least one physically differentiated zone present in an original three-dimensional object.

35

## INTERNATIONAL SEARCH REPORT

Intern. Application No

PCT/GB 94/01427

A. CLASSIFICATION OF SUBJECT MATTER  
IPC 6 B29C67/00 G03C9/08

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 B29C G03C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP,A,0 535 984 (SPECTRA GROUP) 7 April 1993 see column 1, line 1 - line 7 see column 1, line 46 - column 2, line 9 see column 4, line 29 - line 39 ---	1-13
A	GREGORY P. 'High-technology applications of organic colorants' 1992, PLENUM PRESS, NEW YORK cited in the application see page 124 - page 129 see page 215 - page 245 ---	4-10
A	WO,A,90 10254 (BOWLING GREEN STATE UNIVERSITY) 7 September 1990 see page 26, line 25 - line 39 ---	1,2
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☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

## \* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

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"&amp;" document member of the same patent family

Date of the actual completion of the international search

27 September 1994

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# INTERNATIONAL SEARCH REPORT

International Application No  
PCT/GB 94/01427

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>US,A,4 041 476 (SWAINSON) 9 August 1977  see column 12, line 67 - column 13, line 8  -----</p>	1,2

# INTERNATIONAL SEARCH REPORT

Information on patent family members

Inter. Application No

PCT/GB 94/01427

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A-0535984	07-04-93	JP-A- 5212806	24-08-93
WO-A-9010254	07-09-90	US-A- 5137800	11-08-92
US-A-4041476	09-08-77	US-A- 4238840	09-12-80